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PLASMA TORCH  
OXIDATION RESISTANCE AND EROSION  
EVALUATION OF PYROLYTIC MATERIALS

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PLASMA TORCH OXIDATION RESISTANCE AND EROSION  
EVALUATION OF PYROLYTIC MATERIALS

by

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Van Nuys, California

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ABSTRACT

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Pyrolytically derived materials selected for possible use in a free standing liquid propellant rocket thrust chamber were subjected to the effluent of plasma arc heater, which simulated in its composition the combustion products of selected liquid propellants. A principal constituent of this effluent was water vapor (ranging as high as 30%) produced by second stage injection of oxygen into a stabilized nitrogen-hydrogen plasma.

Sample coupons of various pyrolytically derived materials were placed in the arc stream. This report notes the thermal, chemical, and physical effects produced on the test items and compares the materials with each other as candidate materials of construction for the free standing thrust chamber.

HAUGHOR

INTRODUCTION

Many space missions require auxiliary propulsion systems to deliver continuous or intermittent impulses to accomplish such tasks as attitude control, orbital correction, rendezvous, etc. Many of these tasks could be performed with low thrust, hypergolic, liquid propellant rockets. Since the requirements of these systems emphasize long duration operation, minimum system weight, simplicity and reliability, the selection of materials as well as design became a matter of paramount importance. With low anticipated combustion pressures (below 150 psi) and feasibility of complete radiation cooling established, simple, minimum thickness, single wall chambers and nozzles were designed by The Marquardt Corporation.

One of the most unusual structural materials to become available for this application was free standing pyrolytic-graphite. It is formed by the pyrolysis of hydrocarbon vapors on a heated, removable mandrel at reduced pressure. It possesses great, high-temperature strength combined with unique thermal and physical properties. At temperatures above 4000°F where heavier refractory metals lose strength, pyrolytic graphite stands alone with outstandingly high strength-to-weight performance.

With the development of pyrolytic graphite technology, alloys of pyrolytic graphite were developed containing boron, zirconium, molybdenum, tungsten, etc. Pyrolytic carbides and nitrides, as well as pure metals were likewise developed with the result that it became necessary to evaluate and compare these new materials as candidates structural materials for the subject use. Initial screening tests based on subjecting coupons of the

candidate materials to simulated combustion gas effluent of a plasma torch was devised as outlined below.

## II EXPERIMENTAL TECHNIQUES

While a number of refractory metals and ceramics have useful strengths and melting points above the flame temperatures of storable bi-propellants ( $\sim 5000^{\circ}\text{F}$ ), the usefulness of these materials, particularly graphite and tungsten are limited because they are subject to rapid oxidation by the combustion gases of these propellants. It can be shown that these gases can contain more than 30 percent of water vapor. On the other hand typical solid propellant rocket exhaust gases contain less than 10 percent water vapor and usually operate fuel rich. Data in the literature indicates that pyrolytic graphite oxidizes in air at a slower rate than commercial molded graphite. However, most of the available oxidation data is limited to temperatures below  $3000^{\circ}\text{F}$  and to low air flows as in a furnace. Data on oxidation in water vapor at higher temperatures (above  $3000^{\circ}\text{F}$ ) has been totally lacking.

An experimental program was therefore undertaken to measure oxidation rates in high velocity gas streams containing varying amounts of water vapor at sample temperatures above  $3000^{\circ}\text{F}$ . It was also postulated that the pyrolytic deposition technique would render the other refractory carbides and nitrides more resistant to high temperature oxidation than the corresponding pressed and sintered bodies. Samples of such materials were also included in the program.

A. Sample Procurement

A survey of several pyrolytic material vendors was made to determine which materials could be obtained and in what form they would be available. The decision was made to work with free-standing flat samples nominally 1-inch x 1-inch x 0.065-inch thick. Some larger samples of pyrolytic graphite and the boron-pyrolytic graphite alloy were also purchased. Orders were placed for samples of the following materials:

1. Pyrolytic graphite
2. Pyrolytic graphite-boron alloy
3. Pyrolytic graphite-tungsten alloy
4. Boron nitride
5. Titanium nitride
6. Silicon carbide
7. Titanium carbide
8. Zirconium carbide
9. Hafnium carbide
10. Niobium carbide
11. Tantalum carbide
12. High density graphite
13. High density graphite ("heat treated")

Samples of fine grained pyrolytic graphite were obtained from four vendors:

High Temperature Materials, Inc. (HTM)

Raytheon Company

General Electric (GE)

The Beryllium Corporation

Samples of the boron-pyrolytic graphite alloy were received from HTM and Raytheon.

B. Description of Test Specimens

The as-received materials are described in Table I.

The carbides of zirconium, hafnium, columbium, tantalum, and titanium each have face-centered cubic crystal structures. The as-deposited surfaces are similar and show increasingly large crystal growths with increased coating thickness. All of these samples were much more brittle than pyrolytic graphite and boron nitride. They were poorly bonded to the pyrolytic substrate but they may have been more compatible with other substrate materials.

C. Equipment

Measurements of the relative oxidation rates of pyrolytic graphite and the other pyrolytic refractory materials were made in the test rig shown in Figure 1. A Thermal Dynamics Corporation F-40 plasma torch was fitted with a second stage mixing chamber to permit the simulation of rocket combustion products by the injection of controlled amounts of  $H_2$ ,  $O_2$ , or  $N_2$  (Figure 2).

A controlled environment test section was constructed to eliminate oxidation by the atmosphere during heating and cooling of the sample.

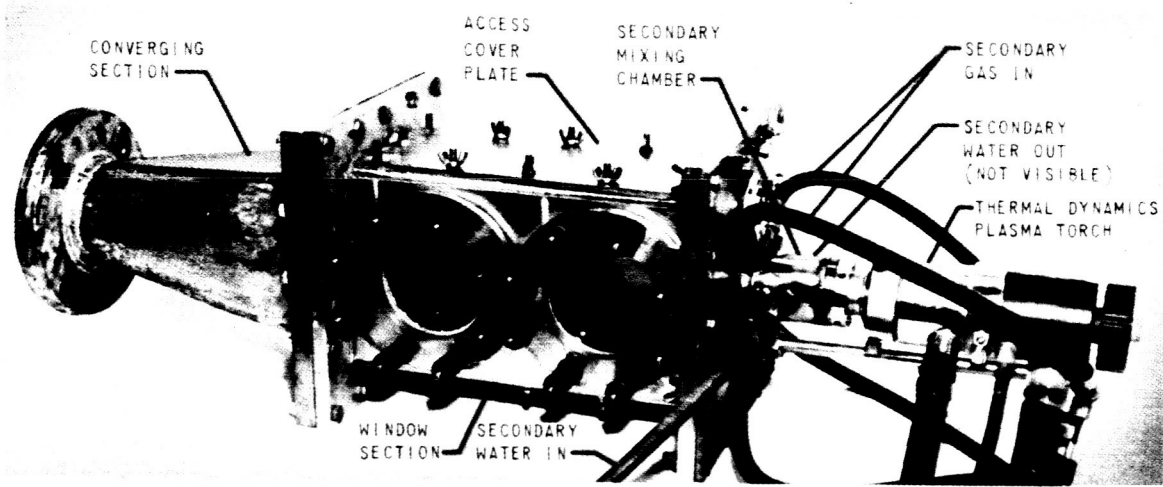


TABLE I

## PYROLYTIC MATERIALS OXIDATION TEST SAMPLES

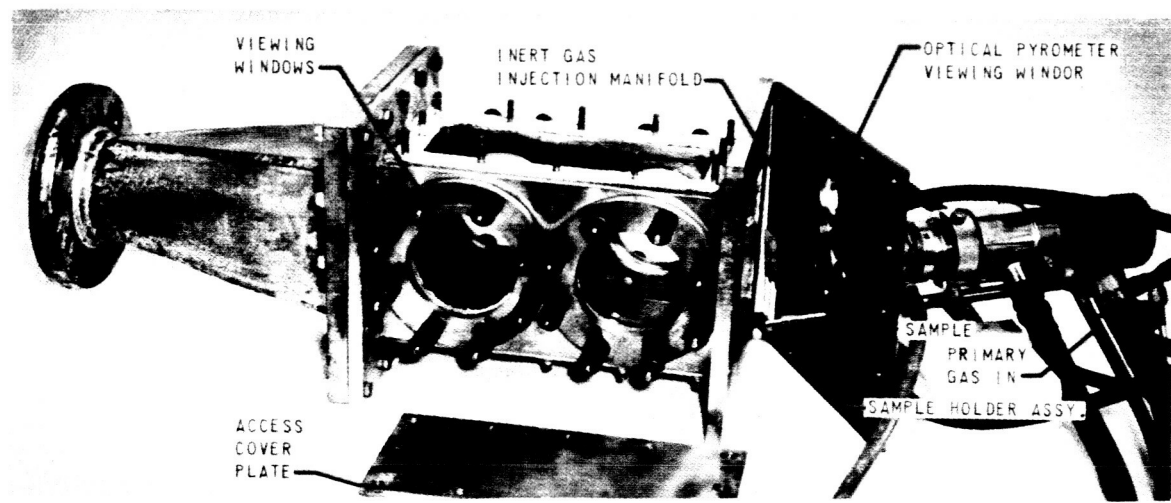
MATERIALS	VENDOR	DESCRIPTION
Boron Nitride MP 5400°F	HTM	Free standing, 10 pieces, 1" x 1" x 0.65", white, smooth
Zirconium Carbide MP 6400°F	Raytheon	Free standing, 3 pieces, 1" x 1" x 0.08", dark grey, large crystals, rough crystalline surface
Hafnium Carbide MP 7000°F	Raytheon	Free standing, 6 irregular pieces, total of 1.5 sq. inch, 0.03 to 0.004 inch thick, rough crystalline surface, bright metallic color
Columbium Carbide MP 6330°F	Raytheon	Coated on PG, 2 pieces, 2.5" x 5.5", 0.25 to 0.30 inch thick on 0.20 PG substrate, poor bond, crazed coating, low bend strength, crumbles, rough crystalline surface, lavender metallic color
Tantalum Carbide MP 7000°F	Raytheon	Free standing, 5 irregular pieces, total of 1.5 sq. inch, 0.015 to 0.020 inch thick, bright metallic, crystalline surface
Tantalum Carbide MP 7000°F	Raytheon	Coated on PG, 4 pieces, 31 sq. inches, 0.003" thick on 0.2 inch PG substrate, poor bond, crazed coating, gold metallic color, smooth crystalline surface
Titanium Carbide MP 5680°F	Raytheon	Coated on graphite, 3 pieces, total of 15 sq. in., 0.005 to 0.070 inch thick, black rough crystalline surface. 3 distinct microstructures in coating build-up from black fibrous base to grey metallic crystals to bright metallic crystals but with black top surface
Titanium Nitride MP 5340°F	Raytheon	Free standing, 5 pieces, irregular shapes, 0.005 to 0.035 inch thick, total of 5 sq. in., gold crystalline structure and surface
Silicon Carbide MP 4350°F	Raytheon	Free standing, 3 pieces, 1" x 1" x 0.20", black, bumpy surface, somewhat fibrous crystal growth, very brittle (broke upon dropping 1.5 inch to hard surface)
Tungsten-PG Alloy	Raytheon	Free standing, 10 pieces, 1" x 1" x 0.080", black, appearance same as PG
High Density Graphite	American Metal Products	10 pieces, 1" x 1" x 0.25", density 1.9 inch (for comparison testing)
Heat treated, high density, graphite	American Metal Products	10 pieces, 1" x 1" x 0.25", density 1.9 inch, surface treated at high temperature

4050-1



A. Assembled View

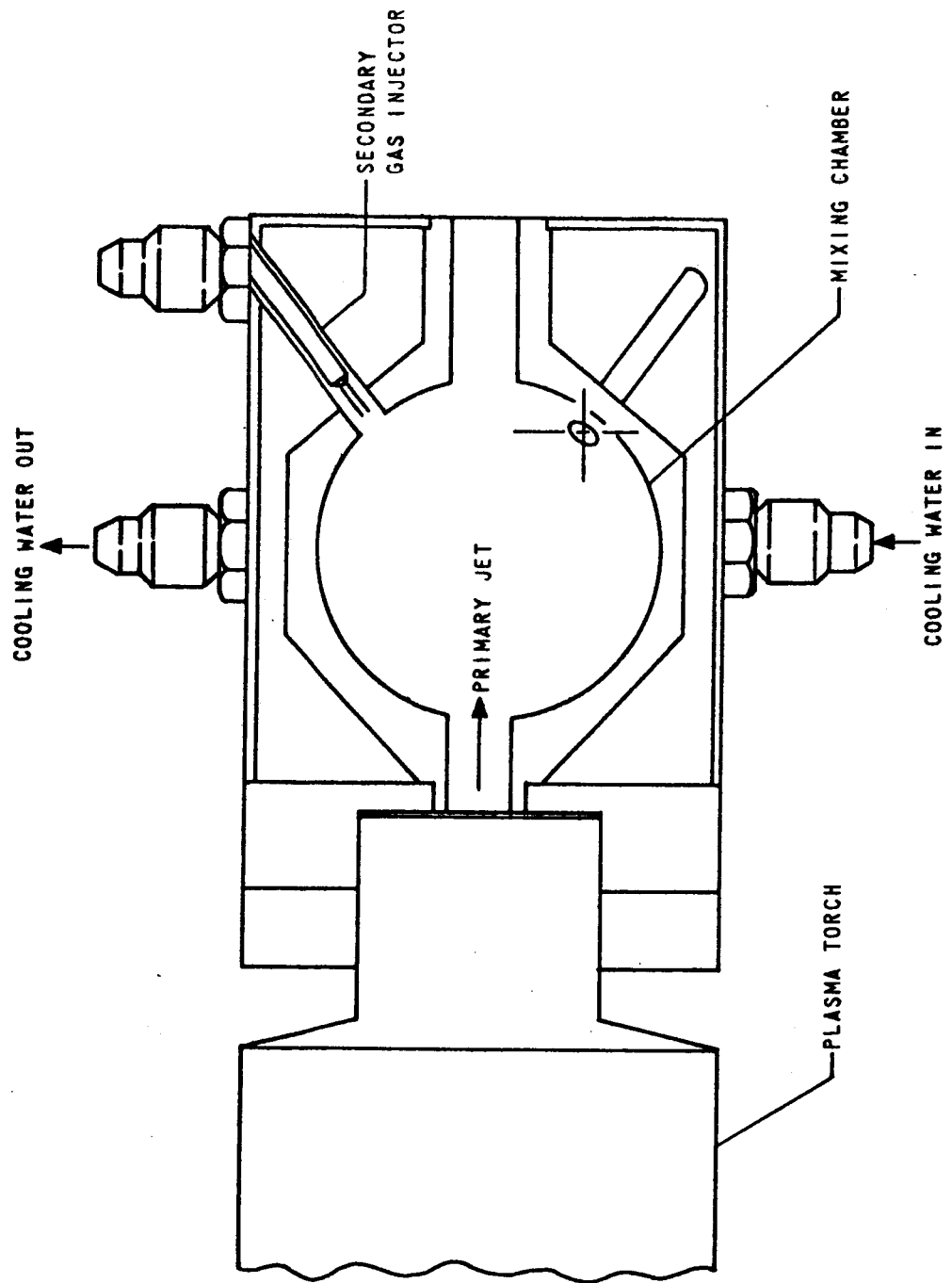
4050-2



B. Disassembled View

Figure 1 - Setup of Plasma Torch Material Testing Apparatus

# SCHEMATIC OF SECONDARY MIXING CHAMBER ASSEMBLY X18032



## D. Procedure

### 1. Oxidation Resistance

Nitrogen or argon was injected into the primary stage of the plasma torch and passed through the high frequency arc. Hydrogen was mixed with the primary gas which allowed operation at a higher power, since for a given current the hydrogen raises the voltage across the arc. The arc heated the plasma to about 10,000°F, then the plasma passed to the mixing chamber where oxygen and/or hydrogen were mixed with the plasma, by injection through the secondary gas injectors as shown in Figure 2. Stoichiometric amounts of hydrogen and oxygen were added to form a specified percentage of water vapor mixed with the inert gas. It could also be run hydrogen "rich" or oxygen "rich" to simulate various propellant mixture ratios.

The chamber was purged with inert gas before, during, and after the oxidation runs through the injection manifold at the test section inlet. The sample was moved into or out of the plasma flame at will using the sample holder, consisting of two zirconium oxide rods mounted in a stainless steel holder. Optical pyrometer temperature measurements of the sample were made during the tests through the viewing window located just above the spray head. The observed temperatures were corrected for emittance using the values shown in Table II\*.

\*Due to limited available data some of these emittance values are only approximate.

TABLE II

SUMMARY OF  
CONDITIONS FOR OXIDATION TESTS OF PYROLYTIC MATERIALS

Sample Run No.	Test Condition	Power (KW)	Primary Weight Flow (pph)			Secondary Flow (pph)		Total Weight Flow (pph)
			A	H <sub>2</sub>	N <sub>2</sub>	H <sub>2</sub>	O <sub>2</sub>	
1 to 27	0% Water Vapor	35.2	13.7	0.50	0	0	0	14.2
1 to 27	10% Water Vapor	33	12.6	0.16	0	0	1.27	14.03
1 to 27	20% Water Vapor	34	11.5	0.32	0	0	2.54	14.36
1 to 27	30% Water Vapor	34	10.5	0.5	0	0	4.00	15.0
1 to 27	50% Water Vapor	30.4	6.19	0.668	0	0.334	5.52	12.69
28 to 51	0% Water Vapor	33	12.6	0.16	0	0	0	12.76
28 to 51	10% Water Vapor	33	12.6	0.16	0	0	1.27	14.03
28 to 51	20% Water Vapor	33	12.6	0.16	0	0.19	2.8	15.75
28 to 51	30% Water Vapor	33	12.6	0.16	0	0.44	4.8	18.0
28 to 51	10% Oxygen	25	8.93	0	1.48	0	1.16	11.57
28 to 51	20% Oxygen	25	8.40	0	1.48	0	2.47	12.35

Sample Distance: 2.0 in. for Runs 1 through 7

0.75 in. for Runs 8 through 51

The standard test sample size was 1" x 1" x 0.065", however, some samples varied in thicknesses as indicated in Table I.. The standard run time was 100 seconds or to perforation of the sample. Each sample was weighted and measured before and after the 100 second runs. Typical sample measurements are shown in Figure 3 for the first seven samples run. Photographs of each sample after testing are shown in Figures 4 through 7. Samples of high density graphite, "heat treated" high density graphite, and pure tungsten sheet were tested for comparison purposes.

The actual torch gas flow conditions are summarized in Table II. Water vapor content was varied from 0 percent to 50 percent and a limited number of tests were conducted with 10 percent and 20 percent oxygen in an argon-nitrogen stream.

The samples of CbC and TaC which were received as coatings on a pyrolytic graphite substrate were not durable enough to be tested satisfactorily with the plasma torch.

Samples of titanium carbide were not received in time to include in this year's program.

## TEST SAMPLE THICKNESS - BEFORE AND AFTER OXIDATION TESTS

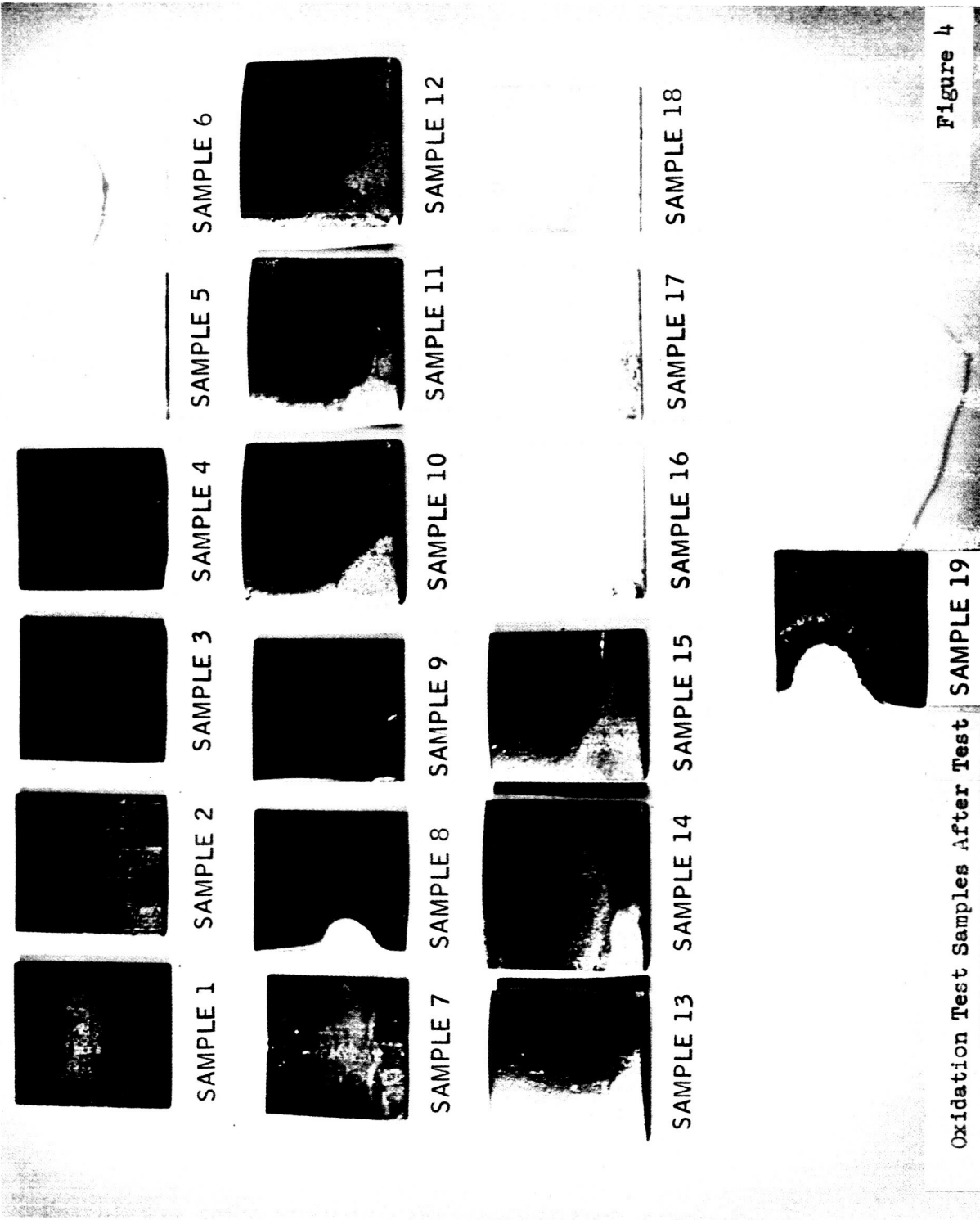
BEFORE FIRING

SAMPLE 1 G.E. - P.G. 0% H <sub>2</sub> O	SAMPLE 2 G.E. - P.G. 10% H <sub>2</sub> O	SAMPLE 3 G.E. - P.G. 20% H <sub>2</sub> O	SAMPLE 4 G.E. - P.G. 30% H <sub>2</sub> O	SAMPLE 5 H.T.M. - BN 0% H <sub>2</sub> O	SAMPLE 6 H.T.M. - BN 30% H <sub>2</sub> O	SAMPLE 7 H.T.M. - B.P. 30% H <sub>2</sub> O
.072 .072 .072 .072 .072	.072 .072 .072 .072 .072	.072 .072 .072 .072 .072	.072 .072 .072 .072 .072	.065 .065 .065 .065 .065	.065 .066 .065 .065 .066	.067 .067 .067 .068 .067
in. wt. - 2.605 gm.	in. wt. - 2.558 gm.	in. wt. - 2.490 gm.	in. wt. - 2.558 gm.	in. wt. - 2.281 gm.	in. wt. - 2.279 gm.	in. wt. - 2.250 gm.

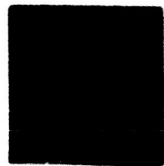
AFTER FIRING

.070 .070 .072 .072 .072	.058 .059 .063 .067 .066	.051 .054 .058 .066 .065	.040 .043 .051 .061 .061	.063 .063 .064 .064 .064	.052 .056 .057 .064 .065	.044 .047 .051 .059 .059
fin. wt. - 2.591 gm.	fin. wt. - 2.129 gm.	fin. wt. - 1.911 gm.	fin. wt. - 1.677 gm.	fin. wt. - 2.228 gm.	fin. wt. - 1.948 gm.	fin. wt. - 1.614 gm.

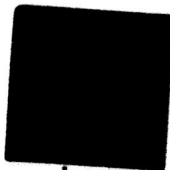
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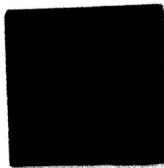




SAMPLE 20



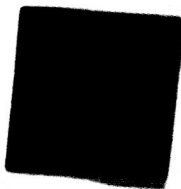
SAMPLE 21



SAMPLE 22



SAMPLE 23



SAMPLE 24



SAMPLE 25



SAMPLE 26



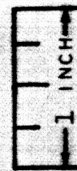
SAMPLE 27



SAMPLE 29



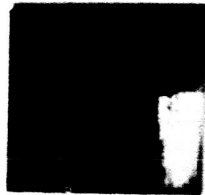
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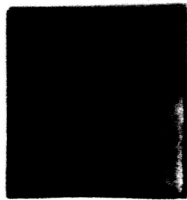
Eroded Samples After High Temperature  
Plasma Jet Tests

Figure 5

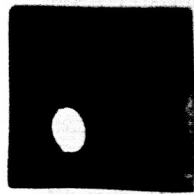
4283-9



SAMPLE 31



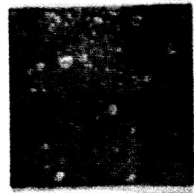
SAMPLE 32



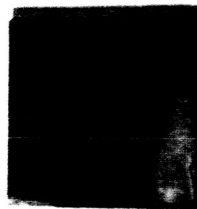
SAMPLE 33



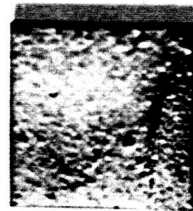
SAMPLE 34



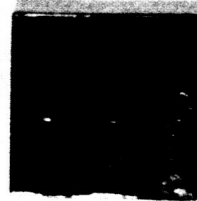
SAMPLE 35



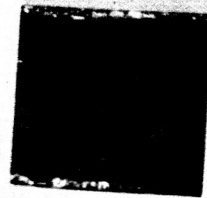
SAMPLE 36



SAMPLE 37



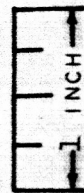
SAMPLE 38



SAMPLE 39



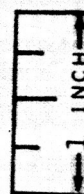
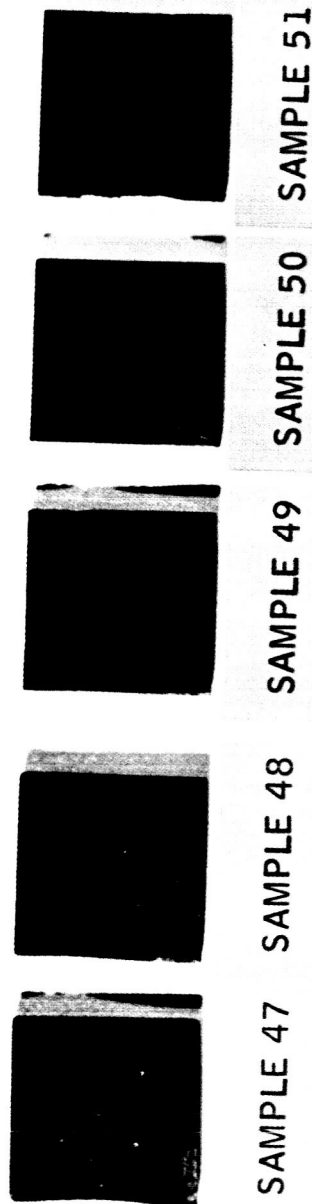
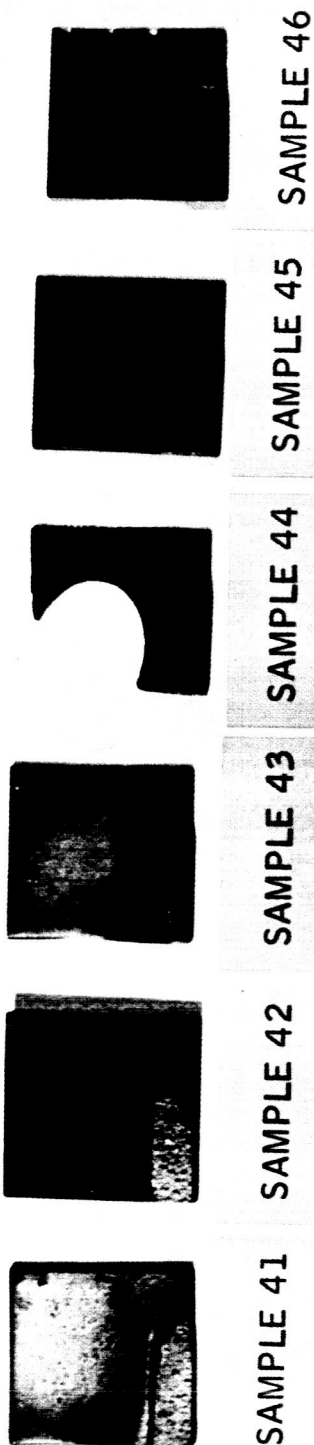
SAMPLE 40



Eroded Samples After High Temperature  
Plasma Jet Tests

Figure 6

4283-10



Eroded Samples After High Temperature  
Plasma Jet Tests

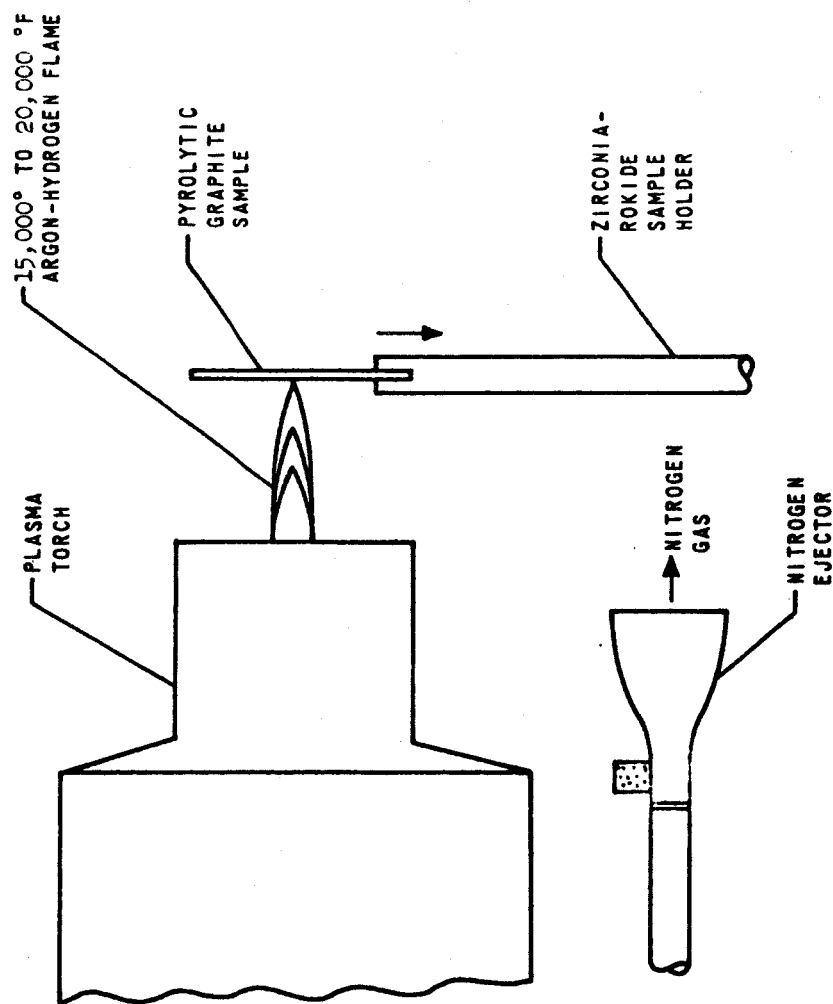
Figure 7

2. Thermal Shock and Delamination Test of a Pyrolytic Graphite Sample

Two additional types of testing were conducted with pyrolytic graphite in the plasma test facility to evaluate thermal shock resistance and the oxidation resistance of edge-oriented pyrolytic graphite.

A thermal shock and delamination test was performed on a 1" x 1½" x 0.07" pyrolytic graphite sample with the test apparatus shown in Figure 8. The plasma torch was operated on 16.8 pounds per hour of argon and 0.314 pound per hour of hydrogen at a power of 30 kilowatts. The flame temperature was estimated to be between 15,000 and 20,000°F. At this condition, it was possible to melt a one-quarter inch diameter zirconia rod in approximately one-quarter of a second at a distance of 1 inch from the nozzle. The pyrolytic graphite sample was held 1 inch from the nozzle for a period of 2 seconds. This time period was used because calculations indicate that the maximum thermal stresses occur for these conditions within the first 2 seconds. During the test, the heated side of the sample achieved an estimated temperature of 6000°F. The sample was then removed from the flame and placed in a stream of cool nitrogen gas to prevent reactions with the atmosphere.

# SCHEMATIC OF THERMAL SHOCK AND DELAMINATION TEST APPARATUS



### 3. Edge-Oriented Pyrolytic Graphite Nozzle Test

Two small scale rocket exit nozzle configurations were fabricated by joining 1" x 1" x 0.125" sheet of pyrolytic graphite together with C-6 graphite cement and machining a nozzle contour with a 0.25" diameter throat as shown in Figure 9. The two nozzle configurations were tested attached to the end of the second stage mixing chamber of the plasma torch and run with a flame containing 30 percent water vapor with temperatures and mass flows equivalent to the flat sample tests. Figure 10 shows the section before and after test.

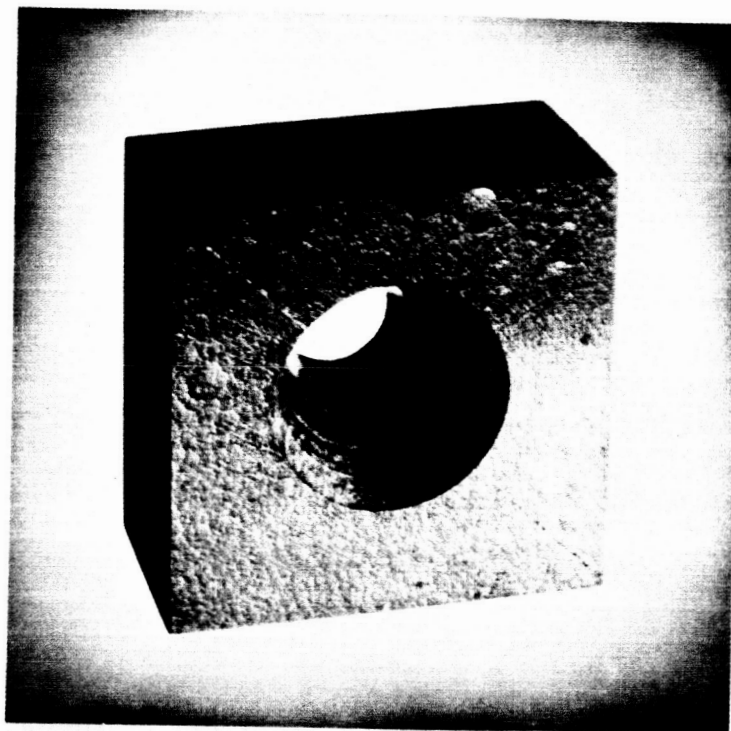
These nozzles were free to radiate laterally and outside wall temperatures were 2200-2900°F.

## III TEST RESULTS AND DISCUSSION

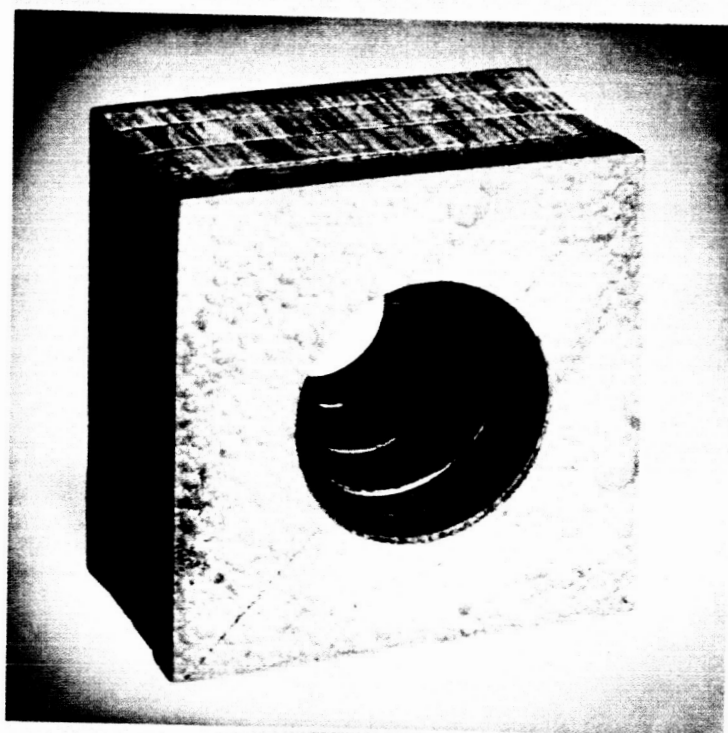
### A. Oxidation Test Results

As a result of the oxidation evaluations conducted during this program, both in torch tests and thrust chamber firings, a clearer understanding of the effective resistance of pyrolytic graphite to the exhaust gas environment of liquid rocket engines has been obtained. The potential improvement in performance of some of the new pyrolytic refractories is also indicated by the oxidation rate comparisons obtained during these tests. The results obtained for each of these materials are discussed in the following paragraphs. Table III summarizes the test results of the oxidation studies.

4050-3



A. Before Test

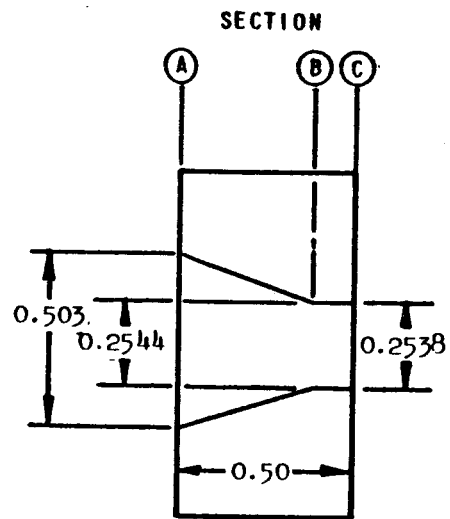


B. After Test

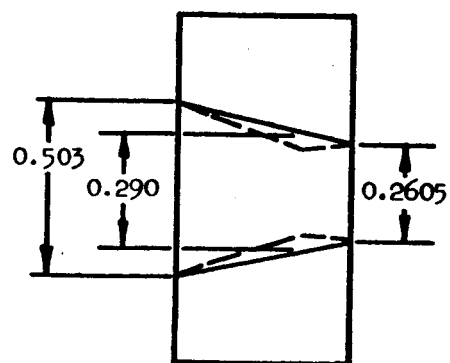
Figure 9 - Rear View of Reoriented Pyrolytic Graphite Nozzle

4050-4

# SCHEMATIC OF REORIENTED PYROLYTIC GRAPHITE NOZZLE



A. BEFORE TEST



B. AFTER TEST



TABLE III

## SUMMARY OF OXIDATION TESTS OF PYROLYTIC MATERIALS

Sample No.	Material	Percent Water Vapor	Sample Temp. (°F)	Run Time (sec)	Weight Loss		Maximum Erosion		Linear Weight Loss Rate (gm/sec)	Maximum Linear Erosion Rate (mils/sec)
					(gm)	(%)	(in.)	(%)		
1	General Electric Pyrolytic graphite	0	3226	100	0.014	0.537	0.0015	2.10	$1.40 \times 10^{-4}$	0.015
2	General Electric Pyrolytic graphite	10.2	3005	100	0.492	16.8	0.0225	31.5	$4.29 \times 10^{-3}$	0.225
3	General Electric Pyrolytic graphite	19.9	3243	100	0.579	23.3	0.0385	53.8	$5.79 \times 10^{-3}$	0.325
4	General Electric Pyrolytic graphite	30.0	3285	100	0.881	34.4	0.0515	72.0	$8.81 \times 10^{-3}$	0.515
5	High Temperature Materials Boron nitride	0	3510	100	0.053	2.32	0.0515	3.08	$5.3 \times 10^{-4}$	0.020
6	High Temperature Materials Boron nitride	30.0	3475	100	0.331	14.5	0.0330	50.8	$3.31 \times 10^{-3}$	0.330
7	High Temperature Materials Boron pyralloy	30.0	3250	100	0.636	28.3	0.0453	67.3	$6.36 \times 10^{-3}$	0.453
8	General Electric Pyrolytic graphite	30.0	4225	50 (Burned through)	1.432	55.3	0.0715	100	$2.86 \times 10^{-2}$	1.430
9	General Electric Pyrolytic graphite	10.2	4028	60	0.993	39.3	0.0475	61.3	$1.66 \times 10^{-2}$	0.792
10	Berylco Pyrolytic graphite	30.0	4176	40	1.092	22.7	0.0550	47.8	$2.73 \times 10^{-2}$	1.375
11	Berylco Pyrolytic graphite	30.0	4176	60	1.712	39.5	0.0860	74.7	$2.85 \times 10^{-2}$	1.43
12	Berylco Pyrolytic graphite	19.9	4176	60	1.051	18.8	0.0580	44.2	$1.21 \times 10^{-2}$	0.667
13	Berylco Pyrolytic graphite	10.2	4130	60	0.725	16.9	0.0400	35.7	$1.21 \times 10^{-2}$	0.667
14	Berylco Pyrolytic graphite	0	4225	60	0.043	0.89	0.0020	1.8	$7.17 \times 10^{-4}$	0.033
15	Berylco Pyrolytic graphite	50	3735	60	0.790	20.3	0.0470	44.7	$1.32 \times 10^{-2}$	0.785
16	High Temperature Materials Boron nitride	30	3655	60	0.697	30.8	0.0370	57.0	$1.16 \times 10^{-2}$	0.616

TABLE III (Continued)

Sample No.	Material	Percent Water Vapor	Sample Temp. (°F)	Run Time (sec)	Weight Loss		Maximum Erosion		Linear Weight Loss Rate (gm/sec)	Maximum Linear Erosion Rate (mils/sec)
					(gm)	(%)	(in.)	(%)		
17	High Temperature Materials Boron nitride	50	3420	40	0.290	12.85	0.0171	26.6	$7.25 \times 10^{-3}$	0.283
18	High Temperature Materials Boron nitride	10.2	4080	60	0.449	19.5	0.0220	33.8	$7.48 \times 10^{-3}$	0.367
19	Raytheon Tungsten Pyrolytic graphite	30.0	3540	50 (Burned through)	1.886	67.0	0.0770	100	$3.14 \times 10^{-2}$	1.540
20	High Temperature Materials Boron Pyralloy	10	3695	60	0.584	26.2	0.034	50.8	0.0097	0.500
21	High Temperature Materials Boron Pyralloy	30	3720	40	0.554	24.6	0.034	50.8	0.0138	0.85
22	High Temperature Materials Boron Pyralloy	50	3575	35	0.600	26.6	0.033	49.3	0.0171	0.943
23	Silicon carbide Run 1 Run 2 Run 3 (Rocket exhaust)	(Plasma nozzle burned out. Sample was soaked with H <sub>2</sub> O)								
		10	2505	445	0.024	0.385	0.007	2.0	$5.4 \times 10^{-5}$	0.0158
		10	3250	100	0	0	0	0	0	0
		Total temperature = 4800°F at exit plane. Sample shattered due to thermal shock								
24	Raytheon Tungsten Pyrolytic graphite	10	3370	60	0.958	33.1	0.030	39	0.0159	0.50
25	Beryllco Pyrolytic graphite	30	4330	100	1.85	40.6	0.091	82	0.0185	0.91
26	Beryllco Pyrolytic graphite	10	4360	100	0.688	13.7	0.040	33	0.00688	0.40
27	Zirconium carbide Substrate	10	4350	100	(Oxide coating formed causing growth of sample)	--	0.010	12.5	--	0.10
28	Titanium nitride	(Weight gain = 0.169 gm, 2.33%. Increase in thickness = 0.010 in., 12.5%)								
		0	4120	100	0.335	100	0.009	100	--	--
(0.009 in. sample backed by graphite)										

TABLE III. (Continued)

Sample No.	Material	Percent Water Vapor	Sample Temp. (°F)	Run Time (sec)	Weight Loss (gm)		Maximum Erosion (in.)		Linear Weight Loss Rate (gm/sec)	Maximum Linear Erosion Rate (mils/sec)
					(gm)	(%)	(in.)	(%)		
29	Hafnium carbide	0	4320	100						
	Substrate	20	4320	50						
	Substrate + Oxide									
30	Hafnium carbide	30	4270	50						
	Substrate									
	Substrate + Oxide									
31	Tungsten	0	3720	100	0.034	0.175	0.001	1.72	0.00034	0.01
32	Tungsten	10	3700	100	6.83	36.1	0.032	55.3	0.0683	0.32
33	Tungsten	20	3700	100	12.41	65	0.058	100	0.1241	0.58
34	Boron nitride	20	3420	100	0.373	16.2	0.023	34.8	0.00373	0.23
35	Boron nitride	20	3900	100	0.668	29.5	0.036	55.4	0.00668	0.36
36	Boron Pyrographalloy	0	3235	100	0.075	1.62	0.016	12.7	0.00075	0.16
37	Boron Pyrographalloy	20	3430	100	0.689	11.2	0.032	19.0	0.00689	0.32
38	Boron Pyrographalloy	20	3635	100	1.168	18.8	0.050	29.2	0.01168	0.50
39	Boron Pyrographalloy	30	3675	100	1.073	21.3	0.051	36.4	0.01073	0.51
40	Boron Pyrographalloy	0	2760	100	0.945	18.8	0.047	31.9	0.00945	0.47
41	Boron Pyrographalloy	0	3185	100	1.683	44.6	0.076	71.0	0.0168	0.76
42	Boron Pyrographalloy	0	2340	100	0.097	1.7	0	0	0.00097	0
43	Boron Pyrographalloy	0	3155	100	2.114	59.4	0.103	100	0.0211	1.03
44	High Temperature Materials Pyrolytic graphite	0	3155	100	1.621	73.5	0.063	100.7	0.0162	0.63

TABLE III (Continued)

Sample No.	Material	Percent Water Vapor	Sample Temp. (°F)	Run Time (sec)	Weight Loss (gm)		Maximum Erosion (in.)		Linear Weight Loss Rate (gm/sec)	Maximum Linear Erosion Rate (mils/sec)
					(gm)	(%)	(in.)	(%)		
45	High Temperature Materials Pyrolytic graphite	0	3225	50	0.964	41.4	0.042	66.7	0.0193	0.85
46	High Temperature Materials Pyrolytic graphite	0	3125	50	0.909	42.1	0.041	65.0	0.0181	0.82
47	American High Density graphite	10	2945	100	0.993	12.85	0.049	19.6	0.00993	0.49
48	American High Density graphite	20	2945	100	0.982	12.8	0.057	22.8	0.00982	0.57
49	American High Density graphite	30	2975	100	1.065	13.9	0.060	24.0	0.01065	0.60
50	American High Density graphite - Heat treated	20	2945	100	0.915	11.57	0.061	24.0	0.00915	0.61
51	American High Density graphite - Heat treated	30	3010	100	1.70	21.6	0.086	33.6	0.017	0.86

Emittance Assumed in Correction of Optical Pyrometer Readings

Material	Emittance
1. Pyrolytic graphite	0.90
2. Boron pyralloy	0.90
3. Tungsten Pyrolytic graphite	0.90
4. Boron nitride	0.40
5. High Density graphite	0.95
6. Silicon carbide	0.88
7. Zirconium Carbide	0.30
8. Hafnium carbide	0.35
9. Tungsten	0.45
10. Titanium nitride	0.50

**NOTES:** Emittance data sources were incomplete for most of the above materials in the temperature ranges required. Many values had to be extrapolated and emittance values were assumed in others where no data were available.

The apparent low values chosen for zirconium carbide and hafnium carbide are due to the fact that oxides built up on the sample immediately, and oxide emittance values therefore were used rather than those appropriate for the carbides.

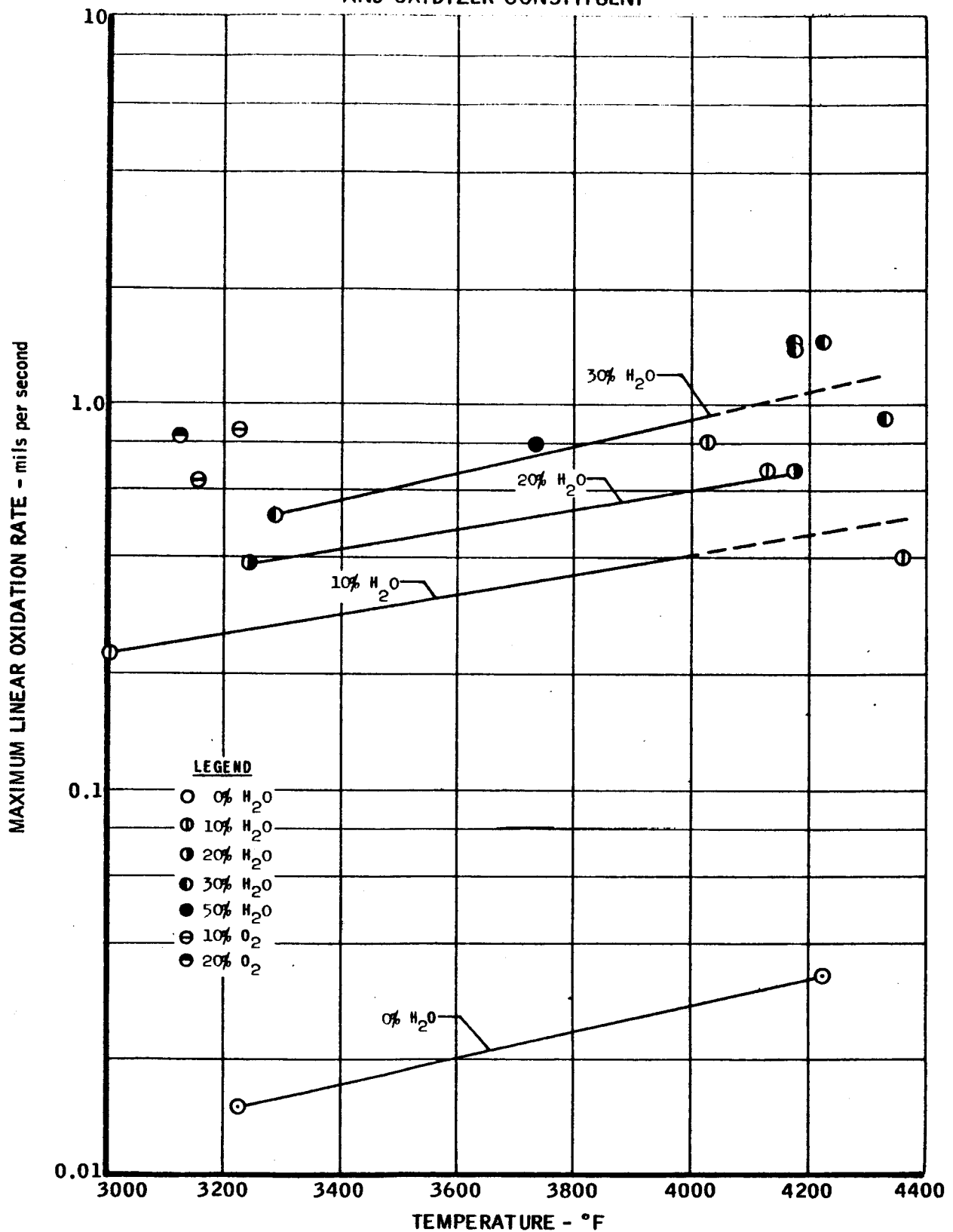
1. Pyrolytic-Graphite (Pyrographite, PG, Anisotropic Impervious Carbon)

Early work with pyrolytic graphite was directed toward its use as a re-entry heat shield material and a coating for graphite in solid propellant rocket exit nozzles. Oxidation and erosion data available from testing in these environments showed pyrolytic graphite to be superior to conventional graphites by a factor ranging from 2 to 10. In some arc torch tests with air, however, pyrolytic graphite showed no clear advantage over other graphites and coatings. Typical erosion rates varied from 0.3 to 0.9 mil/sec for 30 second runs at 5000°F surface temperatures. At 3100°F, erosion rates varied from 0.1 to 0.3 mil sec. Under the same torch conditions, conventional uncoated graphite eroded 3 mil/sec. Marquardt data (Figure 11), for a 20 percent O<sub>2</sub> content gas at a sample temperature of 3100°F, gave an oxidation rate of 0.8 mil/sec.

Initial evaluations of oxidation rates in liquid propellant motors at Marquardt and at the Jet Propulsion Laboratory resulted in values of 0.2 - 0.4 mil/sec. These values seemed to be maxima due to uneven oxidizer-fuel mixing, because, over large areas of the thrust chamber and nozzle, the material experienced oxidation rates of less than 0.1 mil/sec.

When a controlled-water-content gas from the plasma torch was impinged directly on a flat plate of pyrolytic graphite, the resulting oxidation rates as a function of surface temperature

PYROLYTIC GRAPHITE OXIDATION (a-b PLANE)  
 MAXIMUM LINEAR OXIDATION RATE vs. TEMPERATURE  
 AND OXIDIZER CONSTITUENT



and water vapor content were as shown in Figure 11. These rates are generally higher than those experienced in the rocket thrust chambers of free-standing pyrolytic graphite. The data indicate an almost linear increase in oxidation rate with water vapor content up to 30 percent.

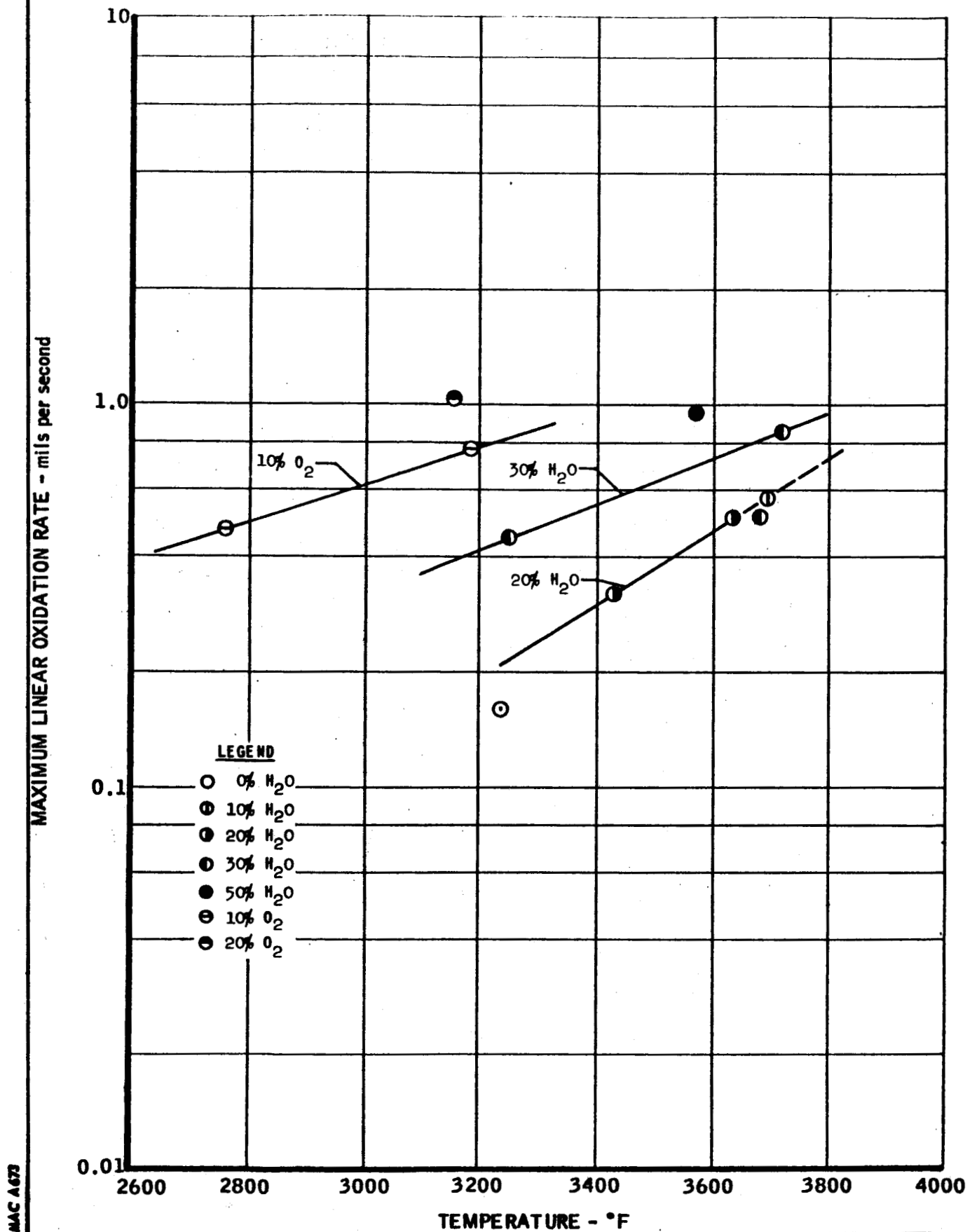
Although surface temperatures were almost uniform over the sample face, the local erosion varied by a factor of 4 over the sample at large. Additional data and analyses are required on the oxidation phenomenon to determine dependence of oxidation rate on gas composition, gas temperature, gas velocity, injector design, and heat transfer.

2. Boron-Pyrolytic Graphite (Boron-Pyrallloy, Boron-Pyrographalloy)

The addition, during deposition, of a small percentage of metallic boron (0.5 to 3 percent) to pyrolytic graphite has an apparent effect on its physical and mechanical properties. Initial strength data indicated that the boron-pyrolytic graphite had a higher room temperature strength than straight pyrolytic graphite. Also early indications were that the oxidation rate was lower.

The Marquardt plasma torch data plotted in Figure 12 shows an oxidation rate of 0.45 mil/sec at 3250°F sample temperature and 30 percent water vapor flame compared to 0.5 mil/sec for pyrolytic graphite at the same conditions. At higher sample temperature, the two materials react the same. Considering

# BORON PYROLYTIC GRAPHITE MAXIMUM LINEAR OXIDATION RATE vs. TEMPERATURE





the data scatter involved, it would be concluded that the boron-pyrolytic graphite alloy has essentially the same oxidation rates at high temperatures as the pyrolytic graphite.

3. Pyrolytic Boron Nitride (BN, Boralloy)

Intermediate temperature data on the oxidation rates of boron nitride in air (Figure 13) shows it to be much more oxidation resistant than pyrolytic graphite. This advantage becomes less at higher temperatures. The data on oxidation rates versus water vapor content and surface temperature is shown in Figure 14, and shows an advantage of boron nitride over pyrolytic graphite at 3400°F but based on the limited data, the oxidation rate for the boron nitride seems to increase faster with temperature than the pyrolytic graphite.

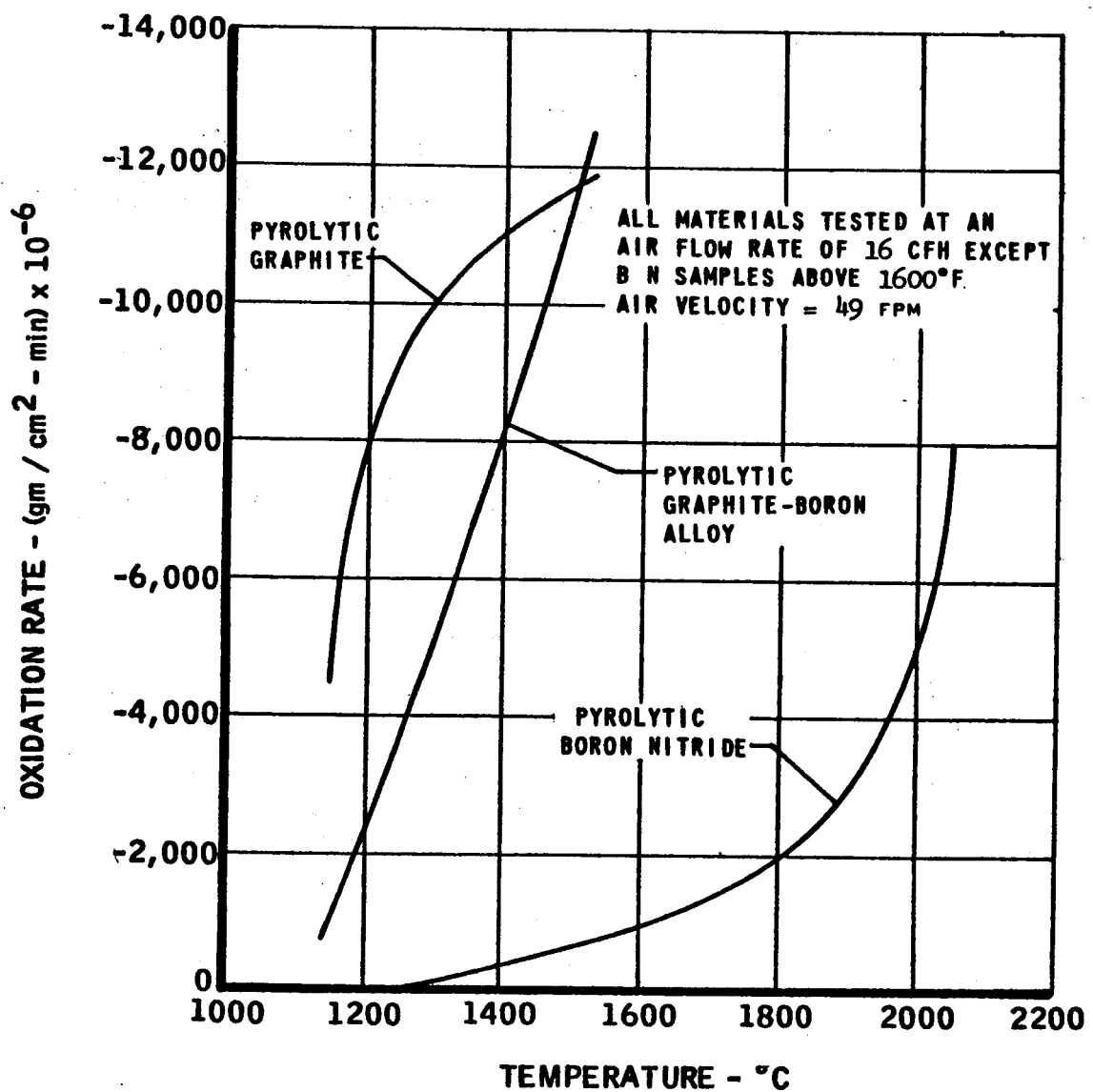
The oxidation rates at 3200°F in a 20 percent O<sub>2</sub> flame are the same for both boron nitride and pyrolytic graphite at 0.75 mil/sec.

4. Tungsten-Pyrolytic Graphite Alloy

Data shown in Figure 15 shows an oxidation rate of 1.5 mil/sec in one test at 30 percent water vapor and 3540°F sample temperature. At 10 percent water vapor the rate is comparable to pyrolytic graphite. The limited data indicates no advantage to the tungsten-pyrolytic graphite with respect to oxidation rate.

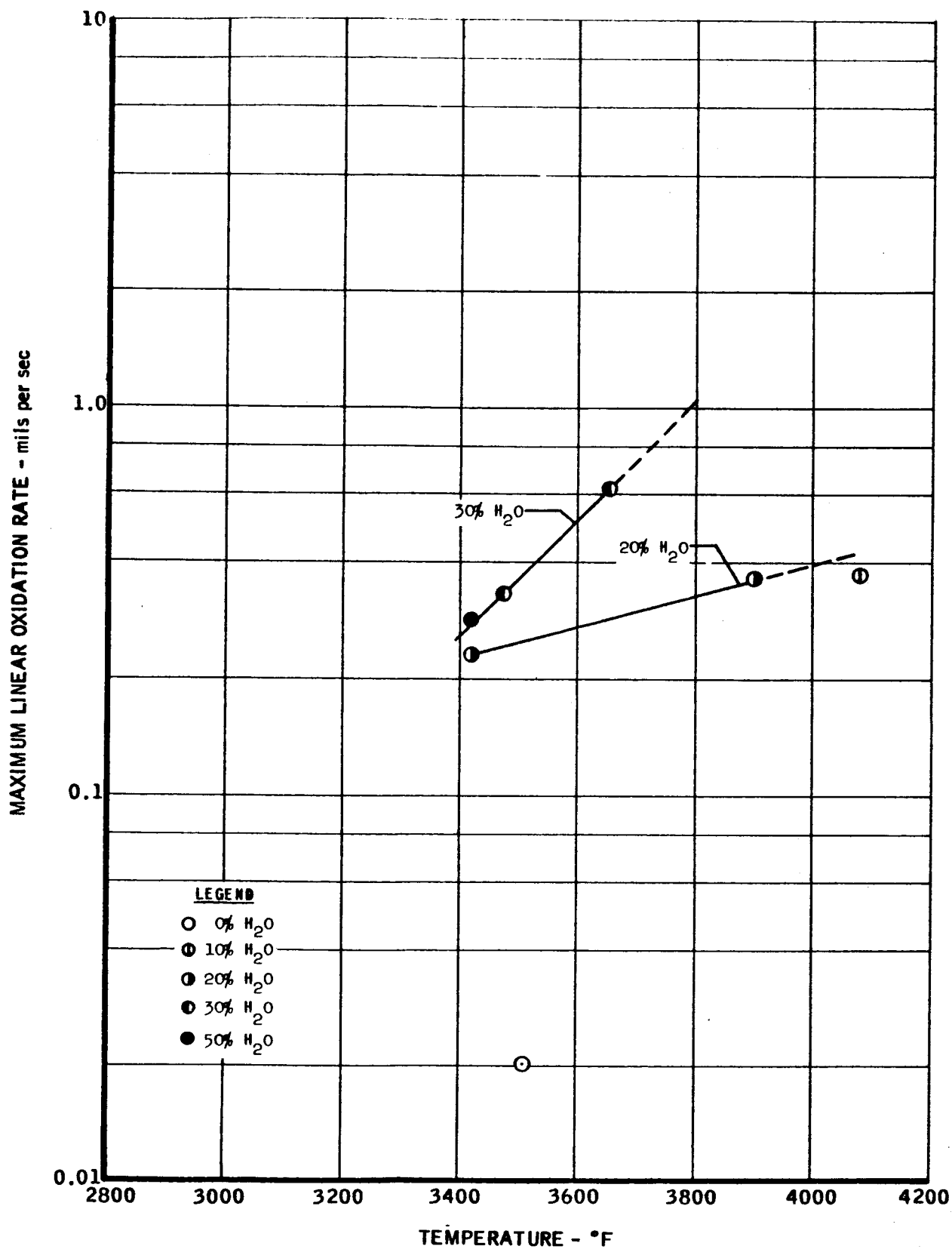
## OXIDATION RESISTANCE OF PYROLYTIC MATERIALS

REFERENCE: PYROLYTIC DEPOSITION OF MATERIALS BY DR. ROMEO G. BOURDEAU,  
HIGH TEMPERATURE MATERIALS INC., BOSTON, MASS.

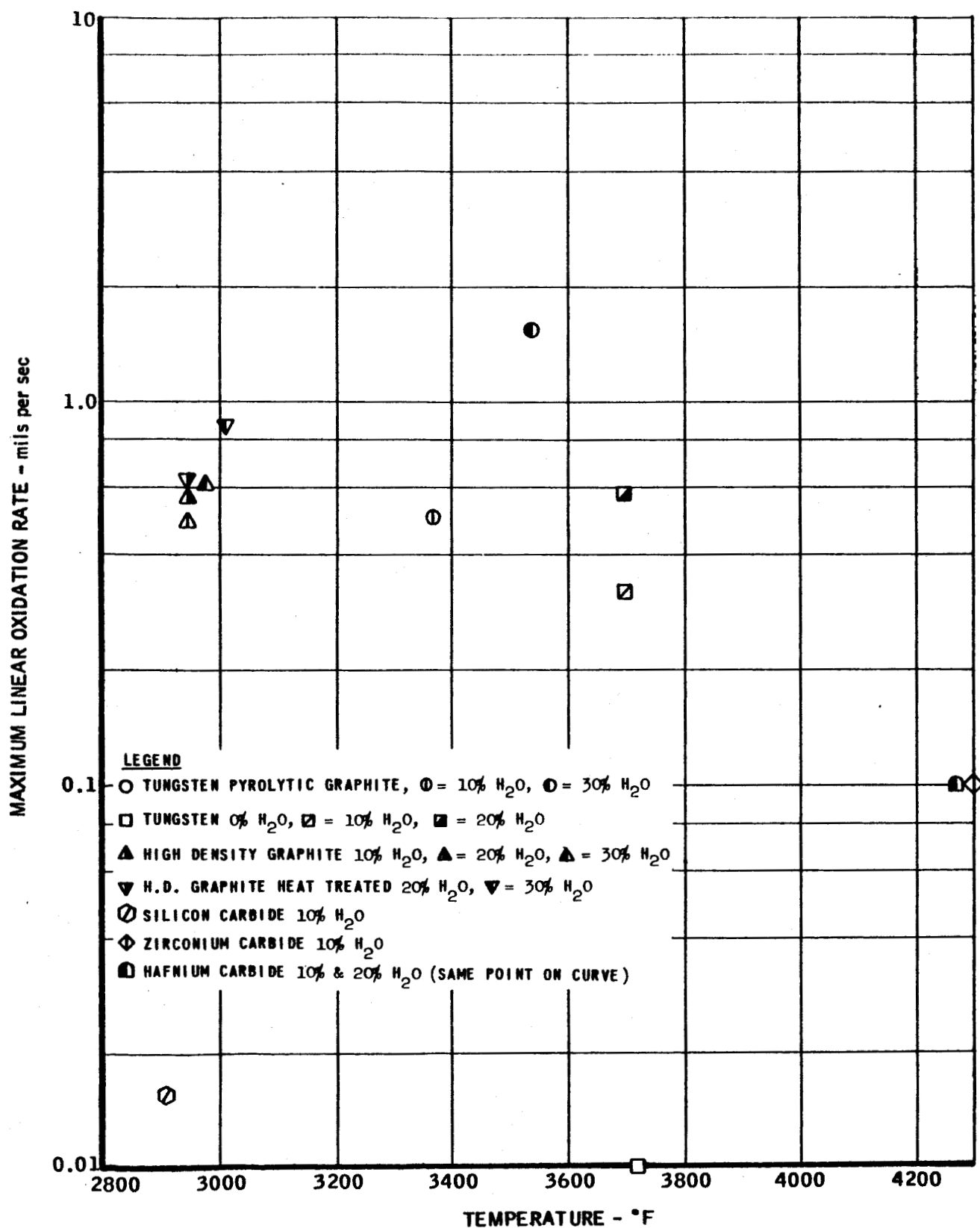


MAC A672

# BORON NITRIDE MAXIMUM LINEAR OXIDATION RATE vs. TEMPERATURE



# PYROLYTIC MATERIALS MAXIMUM LINEAR OXIDATION RATE vs. TEMPERATURE



MAC A673

5. Silicon Carbide

A sample of pyrolytic silicon carbide furnished by Raytheon was tested in the plasma torch with 10 percent water vapor at a surface temperature of 2900°F. The indicated oxidation rate was 0.015 mil/sec for a 445 second run. In order to achieve more severe run conditions, the sample was held in a water cooled sample holder in the exhaust of a  $N_2O_4/0.75$   $N_2O_4-0.25$  MMH rocket firing. The sample cracked early in the run, but remained in the exhaust stream for 34 seconds with negligible surface oxidation.

Exploratory testing of this material in another program, indicates unusual resistance to high temperature even though the material sublimates between 4350°F and 4800°F.

6. Zirconium Carbide and Hafnium Carbide

Zirconium carbide and hafnium carbide both formed stable oxide coatings which adhered during the plasma jet tests. Resultant oxidation rates were low as shown in Figure 15, but this may have been due to the protection afforded by the oxide coating which might spall during actual thrust chamber firing conditions.

7. Titanium Nitride

A 0.009-inch sample of pyrolytically deposited titanium nitride was tested at a 0 percent water vapor plasma condition and complete disintegration of the material was

achieved in something less than the 100 second run duration. A temperature of 4120°F was achieved at the front surface of the sample.

8. Tantalum Carbide

Tantalum carbide, 0.003 inch thick coating on a piece of pyrolytic graphite, was subjected to the water vapor flame. The flame burned through the coating in less than 10 seconds. Edges of the sample showed a conversion of the coating from the carbide to the oxide. The tantalum carbide coating was also subjected to an oxy-acetylene flame and was found to oxidize at surface temperatures of approximately 1600°F as reported in Table IV.

9. Columbium Carbide

The columbium carbide was tested as a coating on pyrolytic graphite. Due to the brittle nature of the coating and poor adherence, it was difficult to keep from spalling the coating before it oxidized. However, at surface temperatures in the 1500-1600°F range, the coating was found to oxidize readily in the oxy-acetylene flame. The results of these tests are summarized in Table IV.

10. Tungsten

Rolled tungsten sheet when tested under the same conditions as the pyrolytic graphite gave similar oxidation rates as shown in Figure 15.

TABLE IV

## OXIDATION AND THERMAL SHOCK EVALUATION OF REFRACTORY COATINGS

## COLUMBIUM CARBIDE AND TANTALUM CARBIDE

Coating Material	Substrate	Gas Used	Temperature (°F)	Behavior
CbC	Pyrolytic Graphite	$\text{CH}_3\text{-O}_2$ (40-60% $\text{H}_2\text{O}$ )	2280° to 2300°	Complete oxidation of coating in 90 seconds.
CbC	Pyrolytic Graphite	$\text{CH}_3\text{-O}_2$ (40-60% $\text{H}_2\text{O}$ )	1650°	Complete oxidation of coating in 112 seconds.
CbC	Pyrolytic Graphite	$\text{CH}_3\text{-O}_2$ (40-60% $\text{H}_2\text{O}$ )	1560°	Complete oxidation of coating in 30 seconds.
CbC	Pyrolytic Graphite	A-H <sub>2</sub> -Air	2900°	Half of coating spalled off almost instantly (1 to 2 seconds). Half of coating oxidized completely on cooling down (10 to 20 seconds).
CbC	Pyrolytic Graphite	A-H <sub>2</sub> -O <sub>2</sub> (30% $\text{H}_2\text{O}$ )	4000°	Coating spalled off instantaneously (1 second).
TaC	Pyrolytic Graphite	$\text{CH}_3\text{-O}_2$ (40-60% $\text{H}_2\text{O}$ )	2010°	Oxidized completely in 105 seconds.
TaC	Pyrolytic Graphite	$\text{CH}_3\text{-O}_2$ (40-60% $\text{H}_2\text{O}$ )	1600° to 1700°	Coating about 1/3 oxidized in 128 seconds.
TaC	Pyrolytic Graphite	A-H <sub>2</sub> -O <sub>2</sub>	4000°	Coating oxidized completely in 10 seconds

B. Test Results - Thermal Shock and Delamination Test of a Pyrolytic Graphite Sample

Low power microscopic examination of the sample after thermal shock testing, as outlined in Section D-3, showed no evidence of cracking or delamination. The only evidence of change was a slightly eroded surface on the heated side of the sample which appeared smoother than before the test. Considering the extreme rate of heating and cooling of the sample, this test is sufficient evidence of remarkable thermal shock resistance for pyrolytic graphite.

C. Test Results of Edge - Oriented Pyrolytic Graphite Nozzle Test

The first nozzle, shown in Figure 10 before and after running for 100 seconds, experienced an average erosion rate at the throat of 0.18 mil/sec.

The second nozzle was 1/8" longer (0.627"). The average erosion rate during a 300 second run was 0.24 mil/sec at the throat and 0.26 mil/sec at an area just ahead of the throat.

IV CONCLUSIONS

Several general conclusions can be drawn from the data presented herein.

- A. Pyrolytic graphite, its alloys, boron nitride and the other pyrolytic materials all oxidize in the presence of water vapor at thrust chamber material operating temperatures.
- B. These oxidation rates increase both with material temperature and water vapor concentration.



- C. Initial oxidation rate testing indicates little advantage of boron-pyrolytic graphite over straight pyrolytic graphite.
- D. Boron nitride, silicon carbide, zirconium carbide, and hafnium carbide exhibit lower oxidation rates in water vapor than the pyrolytic graphites under the test conditions.
- E. Pyrolytic graphite has a high degree of thermal shock resistance under the test conditions.
- F. Erosion tests of edge orientation gave inconclusive results when compared to face orientation of the pyrolytic graphite.
- G. Oxidation rates for normal graphites are 4-10 times as large as for pyrolytic graphite.

V ACKNOWLEDGEMENT

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\*Now with Douglas Aircraft at Santa Monica.